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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of giving gas barrier property to a film.

[0002]

[Description of the Prior Art] Since thermoplastics films, such as a polyamide and polyester, are excellent in reinforcement, transparency, and a moldability, they are used for the application broad as wrapping. However, when using for the application asked for prolonged shelf lives, such as retorting food, still more advanced gas barrier property is required.

[0003] In order to improve gas barrier property, the film which carried out the laminating of the polyvinylidene chloride (PVDC) to the front face of these thermoplastics films has been broadly used for food packing etc., but since PVDC generates organic substances, such as a sour gas, at the time of incineration, while the interest about an environment increases in recent years, shift to other ingredients is desired strongly.

[0004] There is polyvinyl alcohol as an ingredient replaced with PVDC. Although this ingredient does not have generating of a toxic gas, either and the gas barrier property under a low humidity ambient atmosphere is also high, gas barrier property cannot fall rapidly as humidity becomes high, and it cannot use for the package of the food containing moisture etc. in many cases.

[0005] As a polymer which has improved the gas barrier property fall under the high humidity of polyvinyl alcohol, although the copolymer (EVOH) of vinyl alcohol and ethylene is known, in order to maintain the gas barrier property in the high humidity of this polymer on practical use level, it is necessary to make the content of ethylene to some extent high. Since it becomes refractory in water, when considering as a coating ingredient, it will be necessary to use the mixed solvent of an organic solvent, or a water and an organic solvent, such a polymer is not desirable from a viewpoint of an environmental problem, and since it needs the recovery process of an organic solvent etc., it has the problem of becoming cost quantity.

[0006] When using the film which carried out the coat of the polyvinyl alcohol for a retort food packing application further again, it must be deck-watertight-luminaire-ized to the level which can be equal to processing of voile etc. Making the technique deck-watertight-luminaire-ized by various cross linking agents, for example, the polymer containing a maleic-acid unit, react with the hydroxyl group of polyvinyl alcohol conventionally, and being deck-watertight-luminaire-ized is known. For example, having the water resisting property the layer which consists of a 25 - 50% partial neutralization object of an isobutylene-maleic-anhydride copolymer and polyvinyl alcohol excelled [water resisting property] in JP,8-66991,A is indicated. Moreover, the approach of deck-watertight-luminaire-izing the film of polyvinyl alcohol is described to JP,49-1649,A by by mixing an alkyl vinyl ether-maleic-anhydride copolymer to polyvinyl alcohol.

[0007] Furthermore, the approach of constructing a bridge by the ester bond in both polymers is proposed by carrying out the coat of the liquefied constituent which consists of a water-soluble polymer to a film, carrying out the coat of the water solution which consists of a partial neutralization object of

polyvinyl alcohol, polyacrylic acid, or polymethacrylic acid to a film, and heat-treating it as an approach of making gas barrier property high also under high humidity discovering, (JP,10-237180,A). By this approach, the gas barrier property under high humidity is attained by the structure of cross linkage by the ester bond. However, in this system, in order to fully advance an esterification reaction, since heating of long duration was required, the problem was in productivity at the elevated temperature. Furthermore, since a film was put to heat at an elevated temperature for a long time, there was a problem of having colored and spoiling an appearance.

[0008] Moreover, generally the technique of irradiating an electron ray and making the structure of cross linkage forming in a macromolecule is known. For example, the solution which uses polyvinyl alcohol as a principal component is applied to a film, and the approach of improving gas barrier property by irradiating an electron ray is indicated by JP,7-102089,A. However, according to the experiment of this invention persons shown later, most gas barrier property of a film has not improved by such approach. Since polyvinyl alcohol is very a crystalline high macromolecule, also where this is applied to a film, since most molecules were crystallized and the molecule of an amorphism part has also received constraint by existence of the crystal, it is thought that sufficient crosslinking density was not obtained even if it irradiated the electron ray.

[0009] To this problem, the coat of the polyvinyl alcohol is carried out to a base material film, and while a paint film is in a swelling condition, the technique of irradiating an electron ray is proposed by JP,6-143507,A. However, even if it was in the swelling condition, since the crystal of polyvinyl alcohol existed, it did not become essential amelioration, and effectiveness was not seen in the experiment of this invention persons.

[0010]

[Problem(s) to be Solved by the Invention] this invention persons make offer ***** the approach that the thermoplastics film which can maintain high gas barrier property also under high humidity can be manufactured cheaply industrially, to the above problems.

[0011]

[Means for Solving the Problem] Wholeheartedly, as a result of research, this invention persons did the laminating of the coat liquid which consists of a specific resin constituent on the surface of the film, and reached [that the above-mentioned technical problem is solvable and] header this invention by irradiating the electron ray after heat treatment. That is, the summary of this invention is as follows. The manufacture approach of the gas barrier property film characterized by heat-treating at the temperature of 150 degrees C or more, and irradiating an electron ray further after applying at least to one side of a thermoplastics film the solution which contains polyvinyl alcohol (A) and an olefin-maleic-acid copolymer (B) by A/B=97 / 3 - 20/80 (mass ratio) and drying.

[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0013] As a thermoplastics film used in this invention, the layered product of polyolefin resin, such as polyester resin, such as polyamide resin, such as nylon 6, Nylon 66, and Nylon 46, polyethylene terephthalate, polyethylenenaphthalate, polybutylene terephthalate, and polybutylene naphthalate, polypropylene, and polyethylene, the films which consist of those mixture, or those films may be mentioned, and an unstretched film or an oriented film is sufficient.

[0014] As an approach of manufacturing a film, thermoplastics is heated and fused with an extruder, it extrudes from a T die, cooling solidification is carried out with a cooling roller etc., an unstretched film is obtained, or extrude from a circular die, it is made to solidify with water cooling or air cooling, and an unstretched film is obtained. When manufacturing an oriented film, once rolling round an unstretched film, the coincidence biaxial extending method or the approach of extending by the biaxial extending method serially is continuously desirable. The approach of combining the flat type producing-film method and the tenter extending method by the T die from engine-performance sides, such as the mechanical property of a film and thickness homogeneity, is desirable.

[0015] The mass ratio of the polyvinyl alcohol (A) in this invention and an olefin-maleic-acid copolymer (B) needs 97 / 3 - 20/80, and to be the range of 90 / 10 - 40/60 preferably. When separating

from this range, especially, effective crosslinking density for the manifestation of the gas barrier property of the film under a high humidity ambient atmosphere cannot be obtained, and the gas barrier property film made into the purpose of this invention cannot be obtained.

[0016] the polyvinyl alcohol used in this invention -- (A {a polymer (A)}) can obtain the polymer of vinyl ester using completeness or well-known approaches, such as carrying out partial saponification. As vinyl ester, formic acid vinyl, vinyl acetate, propionic-acid vinyl, vinyl pivalate, BASA tic acid vinyl, etc. are mentioned, and vinyl acetate is industrially the most desirable especially.

[0017] It is the range which does not spoil the effectiveness of this invention, and it is also possible to copolymerize other vinyl compounds to vinyl ester. As other vinyl system monomers, partial saturation dicarboxylic acid, such as partial saturation monocarboxylic acid, such as a crotonic acid, an acrylic acid, and a methacrylic acid, and the ester of those, a salt, an anhydride, an amide, nitril, and a maleic acid, an itaconic acid, a fumaric acid, and the salt of those, the alpha olefins of carbon numbers 2-30, alkyl vinyl ether, and vinyl pyrrolidone are mentioned.

[0018] In this invention, in order to give gas barrier property to a film front face, as for the polymer by which a laminating is carried out, it is desirable on production that it is water solubility, and since water solubility will fall if a hydrophobic copolymerization component is made to contain so much, it is not desirable. the vinyl alcohol unit in a polymer (A) -- more than 40 mol % -- containing is desirable. The rate of an ester ligation reaction with a maleic-acid copolymer (B) cannot fall, and the gas barrier film made into the purpose of this invention cannot be obtained except that the above-mentioned water solubility will fall, if the ratio of the vinyl alcohol unit in a polymer (A) is too low.

[0019] In addition, the approach of using the alkali saponifying method well-known as the saponification approach and the acid saponifying method, and carrying out alcoholysis in a methanol especially using hydroxylation alkali is desirable. As for whenever [saponification], it is desirable that it is 80% or more. Although gas barrier property of saponification whenever improves so that it is close to 100%, there is concern which will be gelled if the temperature of a water solution becomes low, and temperature management is needed for preservation. if whenever [saponification] is reduced a little, for example, it is made to about 97% -- the stability of a solution -- markedly -- alike -- increase -- moreover, there is also almost no fall of barrier property ability. on the contrary, barrier property ability falls and **** in the water solubility of a polymer, when whenever [saponification] is too low -- it is divided.

[0020] next, the olefin-maleic-acid copolymer used in this invention -- (B {a polymer (B)}) is obtained by carrying out the polymerization of the olefin monomer to a maleic anhydride by well-known approaches, such as a solution radical polymerization. As an olefin monomer which can be copolymerized, the olefin of the carbon numbers 2-30, such as vinyl ester, such as acrylic ester (meta), such as alkyl vinyl ether to the carbon numbers 3-30, such as the methyl vinyl ether and ethyl vinyl ether, a methyl acrylate (meta), an ethyl acrylate (meta), and butyl acrylate (meta), and formic acid vinyl vinyl acetate, styrene, p-styrene sulfonic acid, ethylene, a propylene, and an isobutylene, etc. is mentioned, and such mixture can also be used. Among these, alkyl vinyl ether and low-grade olefins are the most desirable in respect of improvement in gas barrier property.

[0021] the maleic-acid unit in the polymer (B) in this invention -- more than 10 mol % -- containing is desirable. When a maleic-acid unit is less than [10 mol %], it becomes inadequate forming [of the structure of cross linkage by the reaction with the vinyl alcohol unit in a polymer (A)], and gas barrier property falls. Moreover, this maleic acid may be esterified or amidated partially.

[0022] In addition, in dryness, the maleic-acid unit in the polymer (B) used by this invention tends to serve as maleic-anhydride structure which the contiguity carboxyl group cyclodehydrated, and in the time of humidity, or a water solution, ring breakage of it is carried out and it serves as maleic-acid structure.

[0023] Although the hydroxyl group of a polymer (A) and the carboxyl group of a polymer (B) form the structure of cross linkage by the ester bond with heating and its gas barrier property in high humidity improves High gas barrier property can be made to discover also by short-time heat treatment more by making the cross linking agent (C) which furthermore has (A), (B), or its both and cross-linking contain

at a rate of 0.1 - 20 mass % to the total quantity of (A) and (B). When bridge formation effectiveness with the amount of a cross linking agent sufficient at less than 0.1% cannot be acquired and it exceeds 20%, a cross linking agent will become the inhibitor of gas barrier property, and, in any case, gas barrier property will fall. Although a metal complex with the coordination position of the compound which contains two or more hydroxyl groups or carboxyl groups, and functional groups that react in intramolecular as such a cross linking agent, or many ** etc. is mentioned, desirable things are an isocyanate compound, a melamine compound, an epoxy compound, a carbodiimide compound, a zirconium salt compound, etc.

[0024] As an approach of making a gas barrier layer forming on a thermoplastic film in this invention, the coat liquid which consists of a cross linking agent (C) according to a polymer (A), a polymer (B), and the need is prepared, and it dries after coating on a film, it heat-treats at the temperature of 150 more degrees C or more, crosslinking reaction is advanced, crosslinking density is raised by irradiating an electron ray further, and gas barrier property is raised.

[0025] What is necessary is just to carry out by the well-known approach as the adjustment approach of coat liquid using the dissolution iron pot equipped with the agitator etc. For example, the method of making a polymer (A) and a polymer (B) into a water solution or a water dispersion separately, and mixing and using them before use is desirable. At this time, little addition of alcohol or the organic solvent can also be carried out at water for the purpose, such as compaction of the purpose which raises solubility, or a desiccation process, and an improvement of the stability of a solution. Moreover, the compound used as the catalyst of crosslinking reaction can also be added.

[0026] Furthermore, the gas barrier property of the film obtained can be further raised by carrying out little addition of the stratified inorganic compound of water bloating tendency, such as a vermiculite, and a montmorillonite, hectorite, into the mixture of the polymer (A) in this invention, and a polymer (B).

[0027] In order to raise the gas barrier property of a film enough, as for the thickness of the coat layer which consists of the polymer (A) and polymer (B) in this invention, it is desirable to be referred to as 0.1 micrometers or more.

[0028] Moreover, although the polymer concentration at the time of carrying out the coat of the mixed liquor which consists of a cross linking agent (C) a polymer (A), a polymer (B), and if needed to a film is suitably changed with the viscosity of liquid, or the specification of reactivity and the equipment to be used, it is desirable to make it the range of 10 - 50 mass % of the whole solution. It becomes difficult to carry out the coat of the layer of sufficient thickness to discover gas barrier property as it is too much thin, and it is easy to produce the problem of requiring long duration in a subsequent desiccation process. On the other hand, when the concentration of liquid is too high, a problem may be produced in mixed actuation, shelf life, etc.

[0029] Although especially the approach of coating a film with the mixed solution which consists of a polymer (A) and a polymer (B) is not limited, the usual approaches, such as gravure roll coating, reverse roll coating, wire bar coating, and die coating, can be used. Moreover, coating may be performed before extension of a film and may be performed on the film after extension. Under the present circumstances, in order to make coating nature improve, in advance of coating, corona discharge treatment of the front face of a film may be carried out, or usually well-known processing [coat / acrylic resin urethane system resin, polyvinyl alcohol system resin etc. / as a primer layer] may be performed.

[0030] It may coat, after supplying a tenter type drawing machine, extending and (coincidence biaxial extension) heat-treating a film the transit direction and crosswise at coincidence, after coating an unstretched film first and drying, in order to perform coating in advance of extension, or extending in the transit direction of a film using a multistage hot calender roll etc., and you may extend crosswise by the tenter type drawing machine after desiccation (serially biaxial extension). Moreover, it is also possible to combine extension of the transit direction and the coincidence biaxial extension by the tenter. Moreover, since the method of coating in advance of extension and performing extension and heat treatment after that can use the high temperature at the time of extension and heat treatment for crosslinking reaction, it is a desirable approach.

[0031] In this invention, in order to carry out crosslinking reaction of the polymer (A) and polymer (B) which were formed in one side or both sides of a film, it is desirable to heat-treat in an ambient atmosphere 180 degrees C or more preferably the temperature of 150 degrees C or more. If heat treatment temperature is low, crosslinking reaction cannot fully be advanced, and it becomes difficult to obtain the film which has sufficient gas barrier property. In this way, although gas barrier property of the coating film obtained improves as at least this shows the barrier property which was [but] excellent and increases especially heat treatment time amount, heat treatment of long duration makes productivity fall not much. On the other hand, by the approach of this invention, gas barrier property can be raised to the film which performed a coat, desiccation, and heat treatment much more by irradiating an electron ray.

[0032] The range of 1 - 20Mrad is desirable still more desirable, and the amount of the electron ray irradiated is 1 - 15Mrad. Sufficient bridge formation cannot be introduced as the dose of an electron ray is less than 1 Mrad, but an improvement of gas barrier property is inadequate. Moreover, even if there are too many doses conversely, probably because a chain is cut by too much exposure, gas barrier property falls.

[0033] Although the cause whose gas barrier property improves by irradiating an electron ray in the approach of this invention at a film is not clear, it is thought that the polyvinyl alcohol and the olefin-maleic-acid copolymer which are the principal component of the coat layer of this invention have very high compatibility, the domain of each component is very small even if it is mixing completely or both are not so, and most polyvinyl alcohol is not crystallized. Therefore, constraint of a chain is presumed to be that in which it is few and the structure of cross linkage is easily formed by the electron ray.

[0034]

[Example] Next, an example explains this invention concretely.

[0035] In addition, oxygen transmittance measured the oxygen transmittance in 20 degrees C and the ambient atmosphere of 85% of relative humidity with the Mocon oxygen barrier measuring instrument.

[0036] as example 1 polymer (A) -- made in Unitika Chemical -- polyvinyl alcohol UF040G (whenever [saponification] 99%, average degree of polymerization 400) were dissolved in pure water, and the water solution of 10 mass % was obtained. It is the equimolar copolymer GANTREZ of the methyl-vinyl-ether-maleic acid made from International Specialty Products as a polymer (B). It dissolved in the water solution which contains five-mol % of a sodium hydroxide to the carboxyl group of this polymer, and AN119 was used as the 10 mass % solution. Subsequently, both water solutions were mixed so that the mass ratio of a polymer (A) and a polymer (B) might become 70/30, and it stirred at the room temperature, and coat liquid was prepared. The coat was carried out by MEIYABA so that the paint film thickness after drying this coat liquid on a biaxial extension PET film (Emblet PET 12 by Unitika, Ltd., thickness of 12 micrometers) might be set to about 2 micrometers, and after drying for 2 minutes at 100 degrees C, it heat-treated for 10 seconds at 200 degrees C. The film was introduced into electron-beam-irradiation equipment (the product made from the Nissin high voltage, cure TRON) after that, and 5Mrad(s) (acceleration voltage of 175kV) were irradiated. The oxygen transmittance in 20 degrees C of the obtained film and 85%RH was 81 ml/m2 and day-MPa.

[0037] The oxygen transmittance of the film before irradiating an electron ray in example of comparison 1 example 1 was 150 ml/m2 and day-MPa.

[0038] The exposure of an electron ray was changed like the example 2 and example of comparison 2 example 1, and the film was created. The result was shown in Table 1.

[0039] The same actuation as example of comparison 3 example 1 was performed using the polymer (A). The coated film was created like the example 1 except having used the 10 mass % water solution of the polyvinyl alcohol used in the example 1 as coat liquid. The result was shown in Table 1.

[0040]

[Table 1]

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	ポリマー(A) (質量部)	ポリマー(B) (質量部)	照射量 (Mrad)	酸素透過度 (ml/m ² ·day·MPa)
実施例1	70	30	5	81
実施例2	70	30	10	103
実施例3	70	30	15	140
比較例1	70	30	0	150
比較例2	100	0	5	450

[0041]

[Effect of the Invention] after spreading-drying and heat-treating the coat liquid of this invention at a film so that clearly from an example and the example of a comparison, by irradiating an electron ray further, the gas barrier property of a film can be boiled markedly and can be raised. According to the approach of this invention, the thermoplastics film which has gas barrier property high also under high humidity can be industrially manufactured with sufficient productivity.

[Translation done.]